NATIONAL BUREAU OF STANDARDS REPORT

8932

SOME NEGATIVE IONS FORMED BY ELECTRON ATTACHMENT

by

Robert M. Mills

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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ABSTRACT

The predominant negative ions formed by electron attachment are given for 21 compounds of interest in studying flame inhibition mechanisms. Electron energies used in the ion source are distributed roughly over the same range as those found in a flame, i.e., 0 to 1 ev. The electron bombardment source has cylindrical symmetry and was designed especially for this low energy work.

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A qualititative study has been made of the predominant negative ions formed in an electron bombardment ion source. The compounds used are of interest in the study of flame inhibition mechanisms. The energies of the bombarding electrons in the source are distributed roughly over the same range as those believed to exist in most flames, i.e. 0 to 1 electron volts. A time-of-flight mass spectrometer (1), designed especially for this low energy work, was used to identify the ions.

Figure 1 is a diagram of the ion source. The sample gas is introduced through a leak not shown in the diagram. The source has approximately cylindrical symmetry with a tungsten filament at the center to supply electrons. The first grid surrounding the filament draws the electrons away from the filament. Large, grid-covered windows in the aluminum cap allow electrons through into the circular ionization space between the aluminum cap and the electron collector. This ionization space is nearly field free since the aluminum cap and the electron collector are maintained at the same potential. Thus the energy of the bombarding electrons is determined by the voltage between the filament and the aluminum cap. In this work, the electron energy was adjusted for maximum ion current.

Heating power for the filament is supplied by half-wave rectified, 60-cycle current. During the half cycle when current flows, the I R drop through the filament biases the filament so that electrons do not reach the aluminum cap, thereby reducing the electron energy spread due to the voltage drop across the filament.

Negative ions are drawn out of the ionization region by a small positive voltage on the draw-out grid. They are then focused by three focusing plates shown in the figure. Some electrons are also drawn out and focused on the orifice along with the negative ions, but they are eliminated at the entrance and exit ends of the mass spectrometer drift tube by small permanent magnets. These magnets are not strong enough to deflect the ions. The orifice in Figure 1 helps to maintain the pressure drop between the source (approximately 10^{-3} torr) and the drift tube region (approximately 10^{-5} torr).

The geometry of this source makes it possible to utilize a large fraction of the electrons emitted at any radial angle from the filament and eliminates the need for a collimating magnet. In addition, the cylindrical configuration reduces the space charge problem associated with low energy electrons. The ion current versus electron energy curves go through a sharp maximum which is typical of the electron attachment process, indicating that the ions are produced by the bombarding electrons rather than the interaction of the hot filament surface with the surrounding gas sample. This type of dependence of ion current on electron energy should not exist if the hot filament is responsible for the ionization.

Table I presents the chemical compounds investigated together with the ions identified in this work. Some of the compounds listed have been studied earlier by other researchers. These compounds were included to verify the instrument's performance. Compounds containing more than one halogen usually form negative ions with the heaviest halogen atom. $Fe(CO)_5$, ClO_3F, and $POCl_3$ are distinguished from the others by their forming negative molecular ions after dissociation.

TABLE I: SUMMARY OF RESULTS

SAMPLE	NEGATIVE IONS OBSERVED	SAMPLE PURITY AND SUPPLIER		REFERENCE
1. CCl_4	Cl^-	(Baker 1512)	(B)	(2) (3) (10)
2. CF_2Br_2	Br^-	CF_2Br_2 - 98.9% $CFCl_2Br$ - 1.1%	(M)	
3. CF_2Cl_2	Cl^-	CF_2Cl_2 - 99.8% Hydrocarbons - 0.1%	(M)	(3)
4. CF_3Br	Br^-	CF_3Br - 99.8% C_2HF_5 - 0.1%	(M)	(4)
5. $CHBr_3$	Br^-	Stabilized with Diphenylamine (Eastman 45)	(E)	
6. $CHCl_3$	Cl^-	Spectro Grade (Eastman S 33)	(E)	
7. $CHFCl_2$	Cl^-	$CHFCl_2$ - 99.7%, CCl_3F -0.1% $CHClF_2$ + CH_2F_2 - 0.2%	(M)	(3)
8. CH_2Br_2	Br^-	(Eastman 1903)	(E)	
9. CH_2BrCl	Br^-	(Eastman 5698)	(E)	
10. CH_3Br	Br^-	CH_3Br - 99.7% CH_3Cl - 0.3%	(M)	(5)
11. CH_3I	I^-	(Eastman 164)	(E)	(5)
12. C_2H_4BrCl	Br^-	(Eastman 567)	(E)	
13. C_2H_5Br	Br^-	Ether Free (Eastman 114)	(E)	

TABLE I: SUMMARY OF RESULTS (continued)

SAMPLE	NEGATIVE IONS OBSERVED	SAMPLE PURITY AND SUPPLIER		REFERENCE
14. $C_8F_{16}O$	$C_8F_{16}O^-$	3M Chemical Co. label FC-75 Reported to be a cyclic ether		(6)
15. ClO_3F	ClO_3^- F^-	ClO_3F - 98% Inerts (including Moisture)-2%		(2)(3)
16. $Fe(CO)_5$	$Fe(CO)_4^-$	Obtained from City Chemical Co.		
17. PCl_3	Cl^-	SO_4-0.0005%, Fe-0.0003% Heavy Metals - 0.0005%		
18. $POCl_3$	$POCl_2^-$ Cl^-	SO_4-0.01%, Fe- 0.001% Heavy Metals - 0.002%		
19. SF_6	SF_6^- SF_5^-	SF_6 - 98%	(M)	(3)(7)(8)
20. $TiCl_4$	Cl^-	(Fisher T 308)	(F)	(9)

(B) Obtained from Baker Chemical Co.

(E) Obtained from Eastman Distillation Products Industries.

(F) Obtained from Fisher Scientific Co.

(M) Obtained from Matheson Co.

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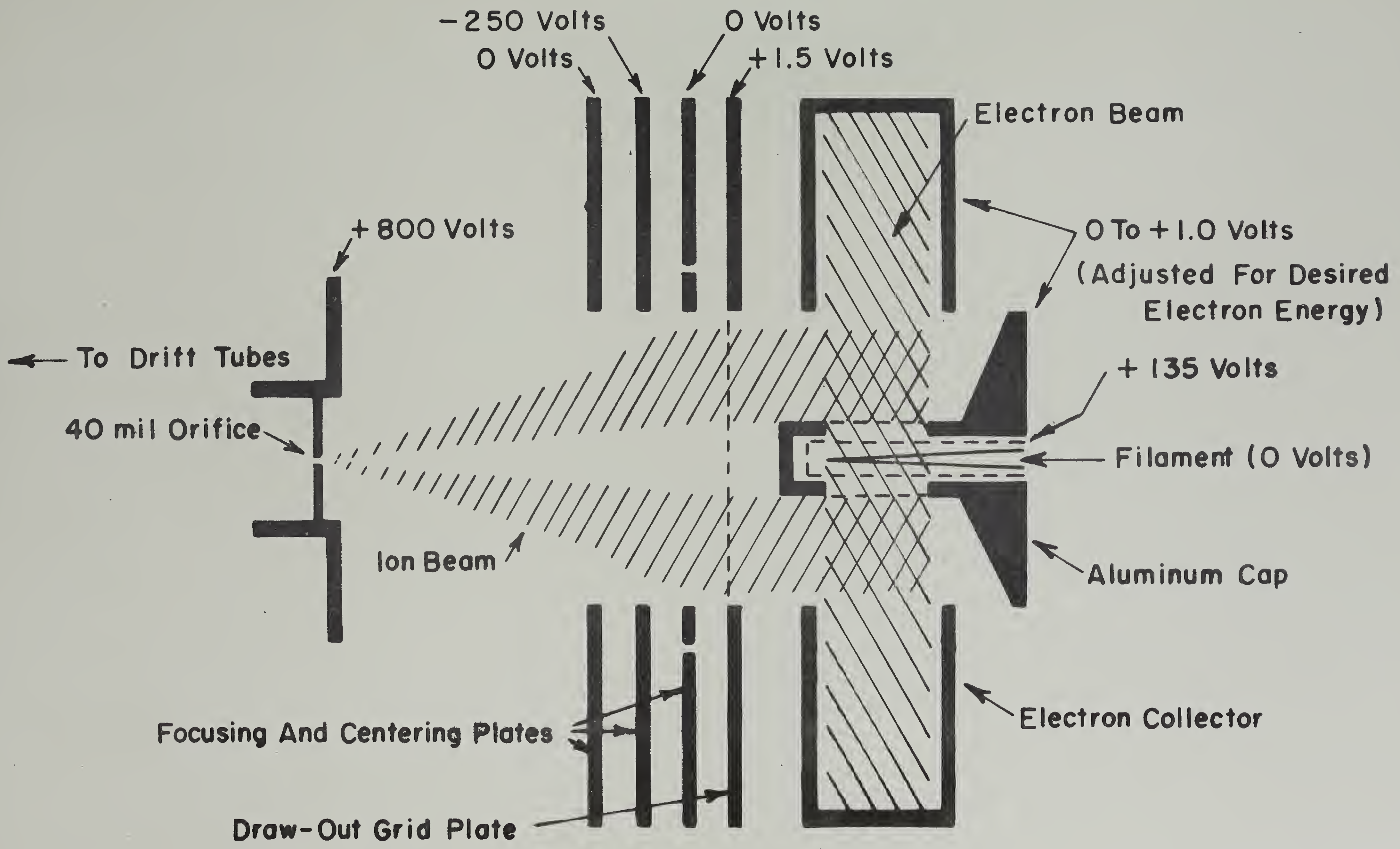

FIGURE I

SKETCH OF ELECTRON IMPACT ION SOURCE

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